

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP2004/008964

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 B01J31/22 B01J37/30 C07F15/00

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01J C07F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, CHEM ABS Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	KOELLE, ULRICH ET AL: "Organometallic aqua complexes. Part 3. Olefin aqua complexes of rhodium(I)" CHEMISCHE BERICHTE, 128(9), 911-17 CODEN: CHBEAM; ISSN: 0009-2940, 1995, XP009044581 cited in the application the whole document	1-6
A	-----	7-13
X	US 6 291 606 B1 (TANG BEN ZHONG ET AL) 18 September 2001 (2001-09-18) column 7, lines 51-55 column 16, lines 45-62 column 17, lines 56-62 claims 1,3,8,10,13,14	1,2,14
A	----- -/--	3-13,15

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*G\* document member of the same patent family

Date of the actual completion of the international search

1 March 2005

Date of mailing of the international search report

14/03/2005

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Goebel, M

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP2004/008964

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 02/36261 A (IMPERIAL CHEMICAL INDUSTRIES PLC; HEMS, WILLIAM, PATRICK; HUTCHINGS, G) 10 May 2002 (2002-05-10) claims	14,15
X	----- BERGBREITER D E ET AL: "Amphoteric, Water-Soluble Polymer-Bound Hydrogenation Catalysts" TETRAHEDRON LETTERS, ELSEVIER SCIENCE PUBLISHERS, AMSTERDAM, NL, vol. 38, no. 21, 26 May 1997 (1997-05-26), pages 3703-3706, XP004064015 ISSN: 0040-4039 cited in the application the whole document	14,15
P,X	----- BATS, JAN W. ET AL: "Low-temperature phase of diaqua(1,5-cyclooctadiene)rhodium(I) trifluoromethanesulfonate" ACTA CRYSTALLOGRAPHICA, SECTION E: STRUCTURE REPORTS ONLINE , E60(1), M85-M87 CODEN: ACSEBH; ISSN: 1600-5368, 2004, XP002319626 the whole document	1-14
P,X	----- HASHMI, A. STEPHEN K. ET AL: "On the enantioselective rhodium-catalyzed enyne cyclization" ADVANCED SYNTHESIS & CATALYSIS , 345(11), 1237-1241 CODEN: ASCAF7; ISSN: 1615-4150, 2003, XP002319627 the whole document	1-14
P,X	----- MOTODA DAI ET EL: "Phosphane-Free Rhodium Catalyst in an Anionic Micellar System for '4+2' Annulation of Dienynes" ANGEWANDTE CHEMIE INTERNATIONAL EDITION, vol. 43, no. 14, 24 March 2004 (2004-03-24), pages 1860-1862, XP002319460 the whole document -----	1,2,14

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP2004/008964

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 6291606	B1	18-09-2001	NONE	
WO 0236261	A	10-05-2002	AU 1247002 A	15-05-2002
			EP 1390142 A2	25-02-2004
			WO 0236261 A2	10-05-2002
			US 2004220049 A1	04-11-2004

## AMENDED CLAIMS

[Received by the International Bureau on 17 May 2005 (17.05.2005)]

Original claims 1-15 unchanged ; new claims 16-20 (3 pages) ]

1. Diene-bis-aquo-rhodium(I) complex of the general formula (1):



where diene is a cyclic diene and X is a noncoordinating anion.

2. Diene-bis-aquo-rhodium(I) complex according to Claim 1, wherein diene is 1,5-cyclooctadiene (COD) or norbornadiene (NBD).
3. Diene-bis-aquo-rhodium(I) complex according to Claim 1 or 2, wherein X is a noncoordinating anion selected from  $\text{BF}_4^-$  and  $\text{CF}_3\text{SO}_3^-$ .
4. Diene-bis-aquo-rhodium(I) complex according to any of Claims 1 to 3 having the name 1,5-cyclooctadienebis(aquo)rhodium(I) tetrafluoroborate.
5. Diene-bis-aquo-rhodium(I) complex according to any of Claims 1 to 3 having the name 1,5-cyclooctadienebis(aquo)rhodium(I) trifluoromethylsulphonate.
6. Diene-bis-aquo-rhodium(I) complex according to any of Claims 1 to 5, wherein the complex is in the form of a solid.
7. Process for preparing a diene-bis-aquo-rhodium(I) complex according to any of Claims 1 to 6, which comprises reacting a rhodium(I)-olefin compound with silver salts in an aqueous solvent mixture, characterized in that the silver salt is not added as a solid to the reaction mixture but is instead prepared in solution and added in this form.

8. Process for preparing a diene-bis-aquo-rhodium(I) complex according to Claim 7, wherein the silver salt is prepared in solution by reacting silver oxide ( $\text{Ag}_2\text{O}$ ) with the acid corresponding to the noncoordinating anion of the diene-bis-aquo-rhodium(I) complex.
9. Process for preparing a diene-bis-aquo-rhodium(I) complex according to Claim 8 wherein the acid is used in an excess of up to 0.5 molar equivalents over the silver oxide.
10. Process for preparing a diene-bis-aquo-rhodium(I) complex according to any of Claims 7 to 9, wherein the preparation of the silver salt is carried out in an aqueous medium.
11. Process for preparing a diene-bis-aquo-rhodium(I) complex according to any of Claims 7 to 10, wherein the rhodium(I)-olefin compound is  $[\text{Rh}(\text{COD})\text{Cl}]_2$ .
12. Process for preparing a diene-bis-aquo-rhodium(I) complex according to any of Claims 7 to 11, wherein the aqueous solvent mixture comprises water together with up to 10% by volume of at least one alcoholic solvent.
13. Process for preparing a diene-bis-aquo-rhodium(I) complex according to Claim 12, wherein the alcoholic solvent is selected from methanol, ethanol, n-propanol, isopropanol, n-butanol and tert-butanol.
14. Use of a diene-bis-aquo-rhodium(I) complex according to any of Claims 1 to 6 in catalytic reactions.
15. Use of a diene-bis-aquo-rhodium(I) complex according to any of Claims 1 to 6 for preparing heterogeneous catalysts.
16. Use of a diene-bis-aquo-rhodium(I) complex according to any of Claims 1 to 6 for preparing a chirally nonselective, diastereoselective or enantioselective catalytically

active species.

17. Use according to Claim 16, wherein the diene-bis-aquo-rhodium(I) complex is reacted with achiral and/or chiral ligands with ligand exchange.
18. Use according to Claim 17, wherein the achiral and/or chiral ligands are selected from triphenylphosphine, ferrocenylphosphine, alkylphosphine or chiral phosphine.
19. Chirally nonselective, diastereoselective or enantioselective catalytically active species, obtainable by reacting a diene-bis-aquo-rhodium(I) complex according to any of Claims 1 to 6 with achiral and/or chiral ligands with ligand exchange.
20. Chirally nonselective, diastereoselective or enantioselective catalytically active species according to Claim 19, wherein the achiral and/or chiral ligands are selected from triphenylphosphine, ferrocenylphosphine, alkylphosphine or chiral phosphine.